# Femtosecond and Nanosecond Laser Irradiation for Microstructure Formation on Bulk Metallic Glass<sup>†</sup>

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KEY WORDS: (Femtosecond Laser), (Nanosecond Laser), (Bulk Metallic Glass), (Microstructure)

### 1. Introduction

Ti-based bulk metallic glasses (BMGs) are expected to be used as new biomaterials because of their high strength, low Young's modulus, and excellent corrosion resistance. Recently, Zhu et al. developed Ti-based BMGs, Ti-Zr-Cu-Pd, without toxic elements, such as Ni, Be and Al<sup>1)</sup>. However, this may not be directly joined to human bones due to their high chemical stability and bioinertness. This can be overcome by surface modification of BMGs<sup>2)</sup> and microstructure formation on BMGs<sup>3)</sup>. For the surface modification and the microstructure formation of BMGs. low temperature processes are more desirable because such processes maintain BMGs' excellent properties. If not, these BMGs will crystallize, resulting in degradation of their properties. Surface modification of BMGs has been developed. It is reported that bioactive titanate nanomesh layers were coated by hydrothermal-electrochemical treatment of BMGs<sup>2)</sup>. This nanomesh layer can induce the growth of hydroxyapatite (HAP), which has good biocompability, in simulated body fluid (SBF). In another surface modification method, it is reported that HAp film was created on titanium plate by aerosol beam irradiation <sup>4)</sup>. These surface modification were performed at low temperature. For microstructures formation on BMGs, the femtosecond laser is a useful tool since it provides considerable advantages for precision material processing, such as drilling, cutting and grooving into the metal <sup>5</sup>) in comparison with nanosecond lasers <sup>6, 7)</sup>. The advantages are based on very rapid creation of vapor and plasma phase, negligible heat conduction, and the absence of liquid phase. It is reported that various microstructures,

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such as periodic nanostructures, periodic microstructures and cone-like protrusions (CLP), are formed on the titanium plate <sup>8,9</sup>. However, microstructure formation on BMGs with the femtosecond laser by controlling the laser fluence and the number of laser pulses has not been investigated yet.

In this study, we reported formation of the microstructures on the BMGs,  $Ti_{40}Zr_{10}Cu_{36}Pd_{14}$ , by femtosecond and nanosecond laser irradiation. The influence of the laser fluence and the number of laser pulses on microstructures was investigated. The experiment for the nanosecond laser irradiation on the BMGs was also carried out. The microstructures formed with the femtosecond laser were compared with the structures produced with nanosecond laser.

### 2. Experimental

A femtosecond Ti:sapphire laser system and nanosecond laser (Nd:YAG) were employed in these experiments. The wavelength, pulse duration, repetition rate, and beam diameter of the femtosecond laser were 775 nm, 150 fs, 1 kHz, and approximately 5 mm, respectively. The laser beam was focused onto the BMG surface by a lens with a 100 mm focal length. The Gaussian laser beam had a diameter of 60  $\mu$ m (at the 1/ $e^2$  intensity points) on the BMG surface. The wavelength, pulse duration, repetition rate, and beam diameter of the nanosecond laser were 1064 nm, about 6 ns, 10 Hz, and approximately 3 mm, respectively. The laser beam was focused onto the BMG surface by a lens with a 150 mm focal length. The Gaussian laser beam had a diameter of 250  $\mu$ m (at the 1/ $e^2$  intensity points) on the BMG surface.

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The BMG's position was controlled with XY stages connected to a computer. An attenuator to reduce the output energy of the laser was composed of polarizing filters.

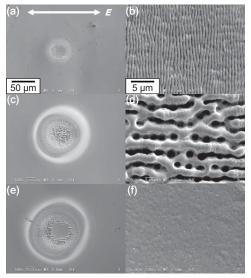
In the first experiment, the BMG surface was irradiated with the femtosecond laser at the average laser fluence of 0.1, 0.5 and 1.0 J/cm<sup>2</sup>, respectively. The number of laser pulses for the irradiation was 100 pulses. In the second experiment, the number of femtosecond laser pulses for the irradiation on the BMG was varied in the range of 10 to 500. The laser fluence was fixed at 0.5 J/cm<sup>2</sup>. In the third experiment, the BMG surface was irradiated with the nanosecond laser at the average laser fluence of 0.6, 1.0 and 1.4 J/cm<sup>2</sup>, respectively. The number of laser pulses for the irradiation was 100 pulses. In the forth experiment, the number of nanosecond laser pulses for the irradiation on the BMG was varied in the range of 10 to 500. The laser fluence was fixed at 1.4 J/cm<sup>2</sup>. The BMG surfaces irradiated by femtosecond and nanosecond laser were observed with a scanning electron microscope (SEM).

### **3. Experimental Results**

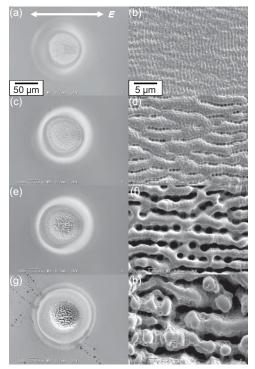
SEM images of BMG surface irradiated with the femtosecond laser for 100 pulses at 0.1, 0.5 and 1.0 J/cm<sup>2</sup> in the first experiment are shown in Figs. 1 (a), 1 (c) and 1 (e), respectively. High magnification images of Figs. 1 (a), 1 (c) and 1 (e), the center region of the irradiation area, are shown in Figs. 1 (b), 1 (d) and 1 (f), respectively. As Fig. 1 (b) shows, the periodic nanostructures, lying perpendicular to the laser electric field polarization vector *E*, were formed in the irradiation area at 0.1 J/cm<sup>2</sup>. The period of the periodic nanostructure was about 600 nm. As Figs. 1 (c) and (d) show, the periodic microstructures, which lay parallel to the laser electric field polarization vector E, were observed in the center region at  $0.5 \text{ J/cm}^2$ . The period of the periodic microstructures (parallel periodic microstructure) was about 2 µm. At 1.0 J/cm<sup>2</sup>, Fig. 1 (e) and Fig. 1 (f) show, the microstructures were not observed in the center region.

In the second experiment with the femtosecond laser, at  $0.5 \text{ J/cm}^2$  for 10, 50, 100, 500 pulses are shown in Figs. 2 (a), 2 (c), 2 (e) and 2 (g), respectively. High magnification images of Figs. 2 (a), 2 (c), 2 (e) and 2 (g), the center region of the irradiation area, are shown in Figs. 2 (b), 2 (d), 2(f) and 2 (h), respectively. As Fig. 2 (b) shows, periodic nanostructures were formed in the irradiation area for 10 pulses. The period of the periodic nanostructure was about 600 nm. For 50 pulses, Figs. 2 (c) and (d) show, the periodic nanostructures were superimposed on the parallel periodic microstructures. The period of the parallel periodic microstructure was about 2 µm. For 100 pulses, Figs. 2 (f) shows the parallel periodic microstructures which were clearly observed compared with those for 50 pulses shown in Fig. 2(d). For 500 pulses, Figs. 2 (g) and (h) show the parallel periodic microstructures which were broken in the center area.

In the third experiment, SEM images of BMG

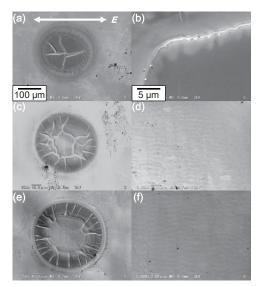


**Fig.1** SEM images of the femtosecond laser irradiation area for 100 pulses at the laser fluence of  $0.1 \text{ J/cm}^2$  ((a) and (b)),  $0.5 \text{ J/cm}^2$  ((c) and (d)) and  $1.0 \text{ J/cm}^2$  ((e) and (f)). (a), (c) and (e) at low magnification and (b), (d) and (f) at high magnification.

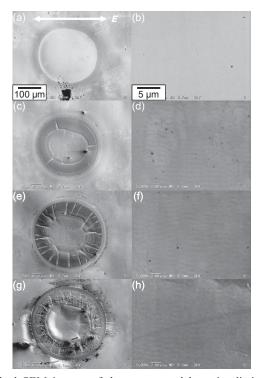


**Fig.2** SEM images of the femtosecond laser irradiation area at 0.5 J/cm<sup>2</sup> for 10 ((a) and (b)), 50 ((c) and (d)), 100 ((e) and (f)) and 500 pulses ((g) and (h)). (a), (c), (e) and (g) at low magnification and (b), (d), (f), and (h) at high magnification.

surfaces irradiated with the nanosecond laser for 100 pulses at 0.6, 1.0 and 1.4 J/cm<sup>2</sup> are shown in Figs. 3 (a), 3 (c) and 3 (e), respectively. High magnification images of Fig. 3 (a), 3 (c) and 3 (e), the center region of the irradiation area, are shown in Figs. 3 (b), 3 (d) and 3 (f), respectively. As Fig. 3 (a) and (b) show, the



**Fig.3** SEM images of the nanosecond laser irradiation area for 100 pulses at the laser fluence of  $0.6 \text{ J/cm}^2$  ((a) and (b)),  $1.0 \text{ J/cm}^2$  ((c) and (d)) and  $1.4 \text{ J/cm}^2$  ((e) and (f)). (a), (c) and (e) at low magnification and (b), (d) and (f) at high magnification.



**Fig.4** SEM images of the nanosecond laser irradiation area at  $1.4 \text{ J/cm}^2$  for 10 ((a) and (b)), 50 ((c) and (d)), 100 ((e) and (f)) and 500 pulses ((g) and (h)). (a), (c), (e) and (g) at low magnification and (b), (d), (f), and (h) at high magnification.

microstructures were not observed at 0.6 J/cm<sup>2</sup>. It was suggested that the BMG surface was melted during the laser irradiation. As Fig. 3 (c) shows, the microstructures were not observed at 1.0 J/cm<sup>2</sup>. It was suggested that BMG surface was melted during the laser irradiation. As Fig. 3 (d) shows, the fringe, which lies parallel to the

laser electric field polarization vector *E*, was observed in the center area. The period of the fringe was about 1  $\mu$ m. As Fig. 3 (e) shows, the microstructures were not observed at 1.4 J/cm<sup>2</sup>. It was suggested that BMG's surface was melted during the laser irradiation. As Fig. 3 (f) shows, the fringe, which lay parallel to the laser electric field polarization vector *E*, was also observed in the center area. The period of the fringe was about 1  $\mu$ m.

In the fourth experiment with the nanosecond laser, at 1.4 J/cm<sup>2</sup> for 10, 50, 100, 500 pulses are shown in Figs. 4 (a), 4 (c), 4 (e) and 4 (g), respectively. High magnification images of Figs. 4 (a), 4 (c), 4 (e) and 4 (g), the center region of the irradiation area, are shown in Figs. 4 (b), 4 (d), 4(f) and 4 (h), respectively. As Figs. 4 (a) and (b) show, the microstructures were not observed in the laser irradiated area. For 50 pulses, Fig. 4 (c) shows the microstructures were not observed. It was suggested that BMG's surface was melted during the laser irradiation. As Fig. 4 (d) shows, the fringe, which lay parallel to the laser electric field polarization vector E, was observed in the center area. The period of the fringe was about 1  $\mu$ m. For 100 pulses, Fig. 4 (e) shows the microstructures were not observed. It was suggested that BMG's surface was melted during the laser irradiation. As Fig. 4 (f) shows, the fringe, which lay parallel to the laser electric field polarization vector E, was also observed in the center area. The period of the fringe was about 1 µm. For 500 pulses, Fig. 4 (g) shows the microstructures were not observed. It was suggested that BMG's surface was melted during the laser irradiation. As Fig. 4 (h) shows, the fringe, which lay parallel to the laser electric field polarization vector E, was also observed in the center area. However, the fringe for 500 pulses was not clearly compared with the fringe for 50 and 100 pulses shown in Fig. 4 (d) and (f). The period of the fringe was about 1 µm. SEM images were unable to measure depth of the peak of the hill to the bottom of the fringe. Measurement of the peak of the hill to the bottom of the fringe is required.

## 4. Summary

We tried to form microstructures on BMGs by femtosecond and nanosecond laser irradiation. For femtosecond laser irradiation, the periodic nanostructures, which lay perpendicular to the laser electric polarization, were formed clearly on the BMG surface at 0.1 J/cm<sup>2</sup> for 100 pulses and at 0.5 J/cm<sup>2</sup> for 10 pulses. For 50 pulses at 0.5 J/cm<sup>2</sup>, the periodic microstructures were superimposed on the parallel periodic microstructures. For 100 pulses at 0.5 J/cm<sup>2</sup>, the parallel periodic microstructures were observed. For 500 pulses at 0.5 J/cm<sup>2</sup>, the parallel periodic microstructures were periodic microstructures were observed. For 500 pulses at 0.5 J/cm<sup>2</sup>, the parallel periodic microstructures were broken.

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